METHOD FOR IMPROVING THE PLASTIC DEFORMABILITY OF HIGH-STRENGTH MOLDED OBJECTS OF SOLID METALLIC GLASSES AND MOLDED OBJECTS PRODUCED THEREWITH

The invention relates to a method for improving the plastic deformability of high-strength molded objects of solid metallic glasses of basic zirconium, titanium and hafnium alloys and to the molded objects produced therewith.

Molded objects of solid metallic glasses with amorphous structure, especially on the basis of early transition metals (zirconium, titanium, hafnium), can be used as new components with a high mechanical stress, such as sports equipment, in the vehicle industry or in the medical area.

It is known that special, multi-component alloy systems, which are also referred to as solid, metallic glasses, can be produced in a metastable glassy state in certain composition ranges in solid form with dimensions greater than 1 mm by conventional casting methods. Aside from iron-based alloys, such alloys are nonferrous-based alloys, especially alloys based on transition metals, such as Pd-Cu-Ni-P, Zr-Cu-Ni-Al, Zr-(Ti, Nb, Pd)-Al-Cu-Ni, Zr-Ti-Cu-Ni-Be, Hf-Cu-Ni-Al, Ti-Ni-Cu-Sn, Cu-(Zr, Hf)-Ti-(Y, Be) (etc., A. Inoue, A. Takeuchi, Materials Transactions JIM 43 (2002) 1892-1906; W.L. Johnson, Materials Science Forum, 35 (1996) 225-227; L.Q. Xing, P. Ochin, M. Harmelin, F. Faudot, J. Bigot, Journal of Non-Crystalline Solids 205-207 (1996) 597-601; L.C. Damonte, L. Mendoza-Zelis, J. Eckert, Material Science and Engineering A278 (2000) 16-21).

It is furthermore known that solid, amorphous molded objects, especially of zirconium-based alloys, have a high-strength (approximately 2 GPa) and a low

modulus of elasticity (approximately 70-100 GPa). However, they have only a limited plasticity (1-2% plastic elongation) in comparison to conventional, polycrystalline materials (A. Leonhard, L.Q. Xing, M. Heilmaier, A. Gerbert, J. Eckert, L. Schultz, Nanostructured Materials 10 (1998) 805-817).

A composition of a multi-component, beryllium-containing alloy with the chemical formula $(Zr_{100-a-b}Ti_aNb_b)_{75}(Be_xCu_yNi_z)_{25}$ is also known. The subscripts a and b refer to the proportions of the elements in atom percent with a = 18.34, b = 6.66 and the subscripts x, y and z refer to the proportions in atom percent with x : y : z = 9 : 5 : 4. This is a two-phase alloy and has a high-strength, a brittle, glassy matrix and a ductile, plastic, deformable, dendritic, cubic space-centered phase. As a result, there is a considerable improvement in the mechanical properties at room temperature, especially in the area of macroscopic elongation (C.C. Hays, C.P Kim and W. L. Johnson, Phys. Rev. Lett. 84, 13, pp. 2901-2904 (2000)). However, the use of the highly toxic beryllium is a serious disadvantage of this alloy.

With the objective of maintaining good plastic deformability while avoiding the use of the beryllium, the addition of certain metallic elements, such as Al, Sn and Sb as alloying elements to molded objects of solid metallic glasses of zirconium alloys and titanium alloys is already known or has already been proposed (DE 102 37 992 A1; DE 102 24 722 C1).

It is an object of the invention to find possibilities for increasing the plasticity and toughness of solid metallic glasses based on early transition metals (zirconium, titanium, hafnium), which are only slight in comparison to the very high-strength, further in order to increase the application potential as a structural material therewith.

This objective is accomplished with the invention presented in the claims.

In accordance with the method provided pursuant to the invention, hydrogen is introduced into the molded objects in a defined concentration range at a concentration below that, at which brittle hydrides are formed.

In this connection, the hydrogen may be brought into the molded objects by means of electrochemical charging in an aqueous electrolyte or by means of a gas-phase reaction.

In the event that electrochemical charging is used, this procedure advantageously is carried out at temperatures ranging from 15°C to 80°C.

When the gas-phase treatment is used, this procedure advantageously may be carried out at 15°C up to 20°K above the glass transition temperature of the respective alloy of the molded object.

The inventive, molded objects, produced with the above-described method, are characterized owing to the fact that hydrogen, homogeneously distributed, is contained in the amorphous short-range order structure and/or in the form of hydrogen-induced local accumulations of ductile alloying components and/or in the form of hydrogen-induced precipitations of ductile nanocrystalline phases with exclusion of brittle hydrides.

Advantageous hydrogen contents range from 20 to 1500 ppm by weight. However, the concentration range depends greatly on the respective alloy composition. Upper limits of 1000 or 800 ppm by weight may also be advantageous.

For beryllium-containing molded objects, a hydrogen concentration ranging from 20 to 650 ppm by weight is provided for pursuant to the invention.

Pursuant to the invention, the hydrogen content may be varied within the limits of the hydrogen solubility in a special alloy, however, only to the extent that brittle hydrides are not formed. Moreover, the hydrogen should be introduced in such concentrations, that a homogeneous distribution of the hydrogen in the amorphous short-range order structure and/or a hydrogen-induced local accumulation of ductile alloying components and/or the precipitation of ductile nanocrystalline phases becomes possible.

Admittedly, it is already known that amorphous alloys, consisting of the early transition metals, such as zirconium and titanium, and late transition metals, such as nickel, palladium and copper and, in particular, consisting of Zr-Ni, Ti-Pd and Zr-Cu, are able to absorb large amounts of atomic hydrogen, which is intercalated interstitially in the atomic, short-range order structure of intermediate lattice spaces with a different energy state (J. H. Harris, W.A. Curtin, M.A. Tenhover, Physical Review B36 (1987) 5784-5797). Previously, this effect has been utilized especially in connection with the creation of high-performance materials for storing hydrogen for fuel cells with the objective of accommodating very large amounts of hydrogen reversibly in the material.

However, this state of the art does not give any hints for accomplishing the objective, on which the present invention is based. Because of the known fact that, when these materials are used for storing hydrogen, there is an appreciable increase in hardness and an embrittlement of the material, someone of ordinary skill in the art would be more likely to regard the use of the element hydrogen for improving the plastic deformability as irrelevant.

With the inventive solution, which is directed to introducing hydrogen in a defined, small amount below the formation of brittle hydrides, an improvement in the macroscopic plasticity and, with that, in the toughness of the materials is achieved in a surprising manner because the plastic deformation energy is increased in comparison to that of the untreated material.

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An improved macroscopic plasticity and toughness is characterized by an increase in the energy of plastic deformation in deformation experiments, which are carried out on amorphous molded objects in the unstressed state and after being charged with hydrogen.

An increase in toughness is associated with a decrease in the breaking stress of hydrogen-charged molded objects in comparison to that of uncharged solid, amorphous objects.

The invention is explained in greater detail below by means of examples.

Example 1

Solid, amorphous, cylindrical molded objects of $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ with a diameter of 3 mm and a length of 6 mm, as well as those with a length of 2 mm were charged electrochemically at room temperature in an alkaline medium of 0.2 M NaOH (+ 0.02 M As_2O_3) at a current density of i = -15 mA/cm^2 with 120 ppm by weight of hydrogen.

After the charging, the hydrogen content of the 2 mm long molded object was analyzed by means of hot gas extraction. Moreover, this molded object was characterized with respect to its microstructure and thermal stability by x-ray diffraction and differential scanning calorimetry.

The mechanical properties of the 6 mm long molded objects were investigated before and after the charging with hydrogen. The energy of plastic deformation in the uncharged state was determined to be 1 MPa in a compression test at deformation rates from 1 to 3 x 10^{-4}/sec. After the charging with nitrogen, the

deformation energy was determined to be 50 MPa. The breaking stress of 2000 MPa in the uncharged state was reduced to 1760 MPA after the charging.

Example 2

Solid, amorphous, cylindrical molded objects of $Ti_{50}Cu_{23}Ni_{20}Sn_7$ with a diameter of 3 mm and a length of 6 mm as well as those with a length of 2 mm were charged electrochemically at room temperature in an alkaline medium of 0.2 M NaOH (+ 0.02 M As_2O_3) at a current density of i = -15 mA/cm^2 with 1000 ppm by weight of hydrogen.

After the charging, the hydrogen content of the 2 mm long molded object was analyzed by means of hot gas extraction. Moreover, this molded object was characterized by x-ray diffraction and differential scanning calorimetry with respect to its microstructure and thermal stability.

The mechanical properties of the 6 mm long molded objects were investigated before and after the charging with hydrogen. The energy of plastic deformation in the uncharged state was determined to be 0.8 MPa in a compression test at deformation rates from 1 to 3 x 10^{-4}/sec. After the charging with nitrogen, the deformation energy was determined to be 600 MPa. The breaking stress of 2100 MPa in the uncharged state was reduced to 1800 MPA after the charging.

Example 3

Solid, amorphous, cylindrical, molded objects of $Hf_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ with a diameter of 2 mm and a length of 4 mm, as well as those with a length of 1.5 mm were charged electrochemically at room temperature in an alkaline medium of 0.2 M NaOH (+

0.02 M As$_2$O$_3$) at a current density of i = -15 mA/cm^2 with 250 ppm by weight of hydrogen.

After the charging, the hydrogen content of the 1.5 mm long molded object was analyzed by means of hot gas extraction. Moreover, this molded object was characterized with respect to its microstructure and thermal stability by x-ray diffraction and differential scanning calorimetry.

The mechanical properties of the 4 mm long molded objects were investigated before and after the charging with hydrogen. The energy of plastic deformation in the uncharged state was determined to be 0.7 MPa in a compression test at deformation rates from 1 to 3 x 10^{-4}/sec. After the charging with nitrogen, the deformation energy was determined to be 85 MPa. The breaking stress of 1800 MPa in the uncharged state was reduced to 1570 MPA after the charging.